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Microwave-assisted pyrolysis and activation of pulp mill sludge

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ABSTRACT

This work analyses the effects of microwaves on the production of char – the solid product of pyrolysis. Using pulp mill sludge and a 1200 W microwave oven, the pyrolysis of the sludge was analyzed and compared with that of conventional heating. Alkali metal hydroxide is an effective microwave absorber; adding a mass fraction of 5% of KOH to dried sludge enabled a complete pyrolysis in a few minutes, compared to hours in conventional pyrolysis. Microwave-assisted pyrolysis, however, retained 20% less carbon from the sludge, likely caused by the faster release of volatiles. The secondary sludge yielded more char than the primary sludge, which may be attributed to its greater protein content. Microwave-assisted combined pyrolysis and activation was feasible, due to the dual roles of alkali metal hydroxides as activating agent and microwave absorber. The combined one-step process generated an activated carbon with a specific surface area of 660 $m^2\ g^{-1}$ from the sludge in three minutes.

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1. Introduction

Pulp mill sludge is a solid waste generated by primary or secondary wastewater treatments in the pulp and paper industry. Primary sludge mainly is composed of wood fibers and fillers, while secondary sludge contains more microbial cells [1]. The Canadian pulp and paper industry produced 3.2 million tonnes of the dry sludge in 2010 [2]. The increased regulations on traditional waste disposal systems call for more effective and environmental friendly alternatives. The cost of waste management in the pulp and paper industry is substantial due to the large quantity of the waste produced every day [3]. Converting the sludge into value added products could reduce the amount of wastes that need disposal while producing economic benefits. Pulp mill sludge has been converted into activated carbon through a two-step process consisting of pyrolysis and chemical/physical activation [4,5]. One possible application of pulp mill sludge-derived activated carbon is for the treatment of pulp mill effluents [6].

Pyrolysis is a thermo-chemical process of converting biomass into gas, liquid and solid products in an oxygen-free atmosphere. Microwave-assisted pyrolysis of biomass is an alternative technology that has received increasing attention in recent years. Microwaves have been reported to improve the pyrolysis process in terms of energy input, cost and processing time [7]. Most of research activities, however, have been focusing on the production of bio-oil and syngas and less on the char [8–10].

Absorption of microwaves by a multi-component material depends on dielectric properties of its components. Some lignocellulosic biomasses are almost transparent to

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microwaves. They require the assistance of microwave absorbers, such as metal oxides, sulphides, carbon-based materials, and silicon carbide, to be heated with microwaves. Microwave absorbers can be mixed with the biomass with the mass fraction between 0.5% and 20% [11–14]. The choice of microwave absorber affects the pyrolysis product yields [15]. The control of product yield remains a challenging task, despite the efforts in improving the effectiveness of microwave-assisted pyrolysis [16]. Moreover, the lack of dielectric properties of biomasses and data from pilot tests, the uncertainty in capital and operating cost have prevented the microwave technology from being widely used [17].

The unique aspect of microwaves is volumetric heating, whereby microwave radiation is dissipated in a dielectric material and the electromagnetic energy is converted directly into heat inside the sample. Consequently, the center of a sample in microwave is at the higher temperature than the surrounding area [17]. It is different from conventional heating where the furnace must reach the higher temperature before the heating of the material starts [18,19]. Thus, microwave heating favors the reactions in solid materials (e.g. devolatilization or heterogeneous reactions) and conventional heating is appropriate for reactions in surroundings, such as homogeneous reactions in the gas-phase. The lower temperature in the microwave cavity can be useful to prevent undesirable reactions [17]. As microwaves generate heat while interacting with materials at the molecular level, selective heating and consequently unique microstructure of the material could be created [20]. Other potential advantages of using microwaves in industrial applications are process simplicity, low energy consumption and rapid start-up [21].

There are also some challenges associated with microwave heating. Electromagnetic field in a microwave oven is not uniform and could cause non-homogenous heating. Physical and structural changes in materials during heating may affect their dielectric properties and consequently cause difficulties in process control and modeling. For example, changes in the dielectric properties of a material with temperature can lead into thermal instability and sample loss [17]. Microwave processing may be further complicated by the variations in chemical composition, size and shape of the material to be processed. All these factors could change the nature of microwave's interaction with the material [22].

This work is focused on the solid product of pyrolysis, char. The objective is to investigate the effectiveness of microwaves radiation in pyrolysis of pulp mill sludge and wood polymers with an alkali metal hydroxide as a microwave absorber. Ultimately, the produced char will be used for production of activated carbon.

2. Materials and methods

2.1. *Materials*

Two pulp mill sludge samples from a northern Ontario mill were used in this work. The samples were collected from daily discharges of the mills, transferred to the lab, and stored at −4 °C prior to experiments. Both samples (PS50-50 and PS70-30) consisted of primary and secondary sludges but at different ratios. PS50-50 contains 50% of primary and 50% of secondary sludge, while PS70-30 contains 70% primary and 30% secondary sludges. The sludge samples were dried overnight at 110 °C in the oven before analysis. The dried sludge was ground to produce powder with particle size of 150–600 μm.

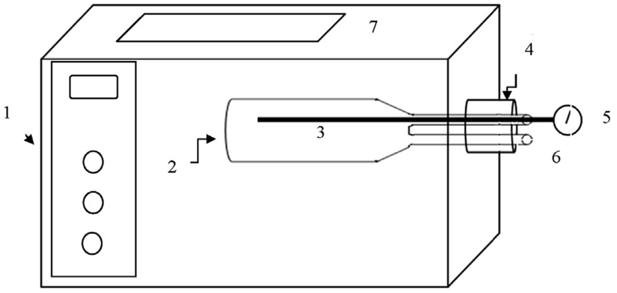

Fig. 1 – Microwave-assisted pyrolysis set up 1-Microwave cavity, 2-Quartz reactor, 3-Capillary column, 4-brass hole and tube, 5-Pressure gauge, 6-outlet for gases, 7-Top magnetron.

Kraft Lignin and cellulose fiber samples were purchased from Sigma–Aldrich (St. Louis, MO, USA) and were used in the pyrolysis studies. KOH and NaOH pellets were purchased from Sigma (St. Louis, MO, USA) and were used as the microwave absorber and activating agent in pyrolysis and activation, respectively.

2.2. *Characterization of two sludge samples*

2.2.1. *Proximate and ultimate analyses*

The total ash and volatile matter of the sludge samples were measured according to ASTM D3174-04 for ash analysis and ASTM D3175-89a for volatiles [23,24]. Total fixed carbon content was calculated by subtracting measured ash and volatile matter contents from the dry sludge weight.

Total carbon, hydrogen, nitrogen, and oxygen elemental content of the pyrolyzed sludge were determined using an Exeter Analytical CE-440 Elemental analyzer. Through quantitative high temperature decomposition, solid substances undergo sublimation to form gaseous mixtures. A 2 mg sample was burned at 1000 °C and the released gases were separated into their components. The elemental contents were determined with a precision and accuracy of up to 0.1%. The carbon contents of pyrolyzed chars were used for the calculation of retained carbon.

Table 1 – Mass fractions of dried pulp mill sludge samples (%).[a]

Samples	Protein	Carbohydrates	Lignin	Extractives	Ash
PS50-50	20	45 ± 5	15 ± 4	16 ± 5	4
PS70-30	8	48 ± 3	23 ± 2	18 ± 4	4 ± 1

[a] Standard Deviation (SD) is not reported when it is lower than 1.

Table 2 – Proximate and ultimate analyses of dried pulp mill sludge samples.[a]

Raw materials	Proximate analyses (%)			Ultimate analyses (%)				
	Fixed carbon	Volatile matter	Ash	C	H	N	O	Others
PS50-50	13 ± 1	82 ± 1	4	51 ± 2	6 ± 1	3	25	14
PS70-30	18 ± 1	77 ± 2	4 ± 1	46	6	8	21	19

[a] Standard Deviation (SD) is not reported when it is lower than 1.

2.2.2. *Extractives, carbohydrates, lignin, and protein measurements*

The sludge samples were analyzed for their constituents. Extractives are composed of monoterpenes, phenolics, fatty acids, resin acids, resin acid neutrals and sterols. The extractive content was measured based on the procedure presented in the TAPPI Standard T 264 cm-07 [25]. Carbohydrate fraction includes both cellulose and hemicellulose. The cellulose and hemicellulose contents of the extractive-free sludge were determined by a procedure developed by Ref. [26]. In this method, 0.7 g of extractive free sample was treated with 10 cm^3 of glacial acetic acid, 20 g sodium hydroxide, and 1 cm^3 chlorite solution. The samples were placed in a 70 °C hot water bath for 4 h. The remaining solids were washed with acetic acid and acetone to remove the moisture. The dried samples were weighted to determine the final percentage of holocelluloses (cellulose and hemicelluloses) [26].

Klason lignin was measured by following the TAPPI standard T 222 om-11 method, which is based on acidic digestion of polysaccharides in sample [27]. Total protein in sludge samples were measured using the Kjeldahl method [28].

2.3. *Microwave-assisted pyrolysis set-up*

Fig. 1 shows the set-up for microwave-assisted pyrolysis. A 1200 W industrial microwave oven (Panasonic NE1257) with two magnetrons (top and bottom) was used for pyrolysis. The oven was operated at the frequency of 2.45 GHz. The cavity of the microwave oven had a size of 30 × 30 × 18 cm. A hole of ~3 cm in diameter was created on a side wall of the oven, for inserting a 10 cm-long brass tube. Since the size of the opening on the cavity was smaller than one third of the microwave wavelength (12 cm), the microwaves are not expected to leak.

For pyrolysis, samples were placed in a quartz reactor with dimensions of 12 cm long and 5 cm inner diameter. Quartz is transparent to microwaves and cannot be heated by microwaves. The reactor had two openings made of 10 cm-long quartz tubes. The inner diameter of the tubes were 0.5 cm. The openings were used for multiple purposes – introducing nitrogen gas to purge the reactor at the beginning of pyrolysis, releasing gases/volatiles produced from the sample during pyrolysis and/or inserting the capillary pressure probe when the temperature of the sample needed to be measured. Details of the temperature measurement were described by Namazi et al. [29]. After loading the sample to the reactor, the reactor was fixed inside the oven which was placed in a fume hood. The two openings of the reactor were connected to plastic tubing and sealed with a high-temperature vacuum grease.

In every experiment, the quartz reactor was packed with 20 g of dried and ground sludge sample. The sludge samples were homogenously mixed with 1–5% powdered KOH as the microwave absorber. KOH pellets were ground for 1 min with a coffee grinder. The particle size of KOH after grinding was in the range of 300–600 μm. The uniformity of KOH-sludge mixture was critical to a uniform char product. Samples of pulp mill sludge were pyrolyzed in the reactor under various conditions (time: 3–10 min; power levels: medium-600 W and high-1200 W). The char product was cooled down to room temperature with the reactor and discharged for subsequent analysis. To measure temperature, the pressure probe was inserted into the sludge sample inside the quartz reactor through one of two openings on the reactor [29].

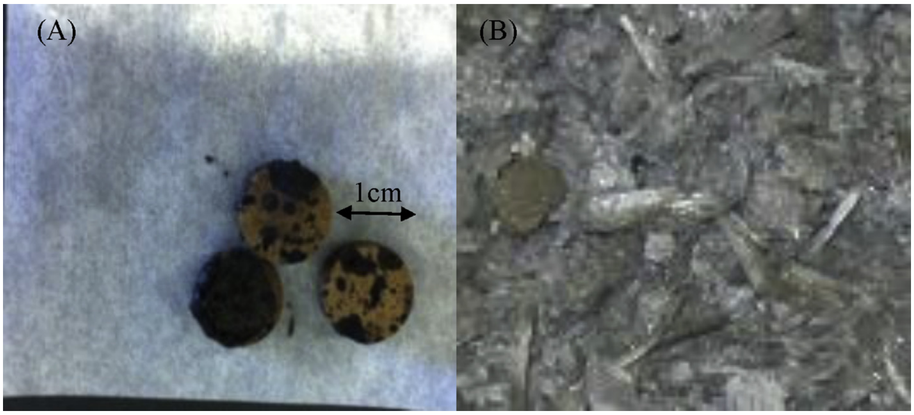

Fig. 2 – Pellet (A) and powdered (B) of the pulp mill sludge after addition of 1% KOH and three min microwave-assisted pyrolysis.

Microwave-assisted pyrolysis experiments were designed to test the effect of sludge composition, sample shape, and ratio of microwave absorber (KOH) on char production. To study the effect of biomass shape, two grams of powdered samples were pressed into small disk-shape pellets with a diameter of 1 cm and a height of 0.4 cm. The pellets were made of dried sludge, lignin and cellulose, respectively. The density of the powdered and pellet sludge samples were calculated by dividing the mass of the sample to its volume.

For comparative purposes, pyrolysis of pulp mill sludge, cellulose and lignin were also conducted in an electric furnace. For consistency in the experiments, mass fraction of 5% KOH was added to the dried, powered samples. The effect of pyrolysis time from 1 to 4 h on retained carbon (%) at 400 °C was studied. The effect of sample shape i.e. pellet or powered was analyzed for lignin, cellulose and sludge samples in the temperature range of 400–800 °C.

To quantify the effectiveness of pyrolysis, the pyrolysis yield and the retained carbon are used. As shown by the equations of 1 and 2. The yield is the percentage of dry sludge that has been converted into char after pyrolysis. The retained carbon is the percentage of carbon in the char that is retained after pyrolysis of sludge.

$$\text{Pyrolysis Yield } (\%) = \frac{\text{Mass of char (carbon + ash)}}{\text{Mass of dried raw material}} \times 100 \qquad (1)$$

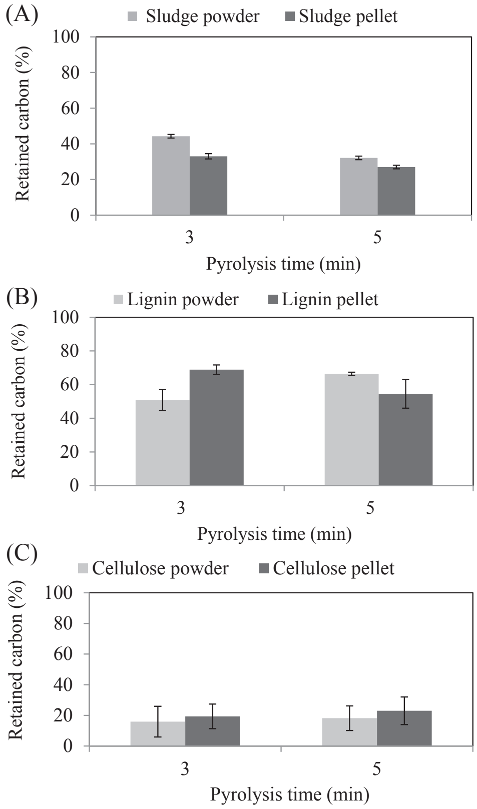

Fig. 3 – Retained carbon (%) from sludge (A), lignin (B) and cellulose (C) in microwave pyrolysis with the power of 1200 W and 2 g sample.

$$\text{Retained carbon } (\%) = \frac{\text{Pyrolysis yield}(\%) \times \text{Mass fraction of carbon}(\%)\text{in char}}{\text{mass fraction of carbon in raw material } (\%)} \qquad (2)$$

An alkali metal hydroxide, i.e. KOH, was used as a microwave absorber for pyrolysis, since they are also commonly used as activating agent for activated carbon production. Moreover, the combined pyrolysis and activation was tested with NaOH. Both KOH and NaOH are good microwave absorbers for microwave pyrolysis. While KOH is well known for its effectiveness in creating porosity in carbonaceous materials, NaOH has been used to chemically activate carbonaceous material and is much cheaper than KOH. NaOH is also readily available in Kraft mills [29]. The activated carbon was produced by mixing 5 g of dried and ground sludge with NaOH pellets with the NaOH: sludge weight ratio of 1:1 and 1:2. The particle sizes of ground NaOH were between 300 and 600 μm. The homogenous mixture of powdered sludge and NaOH was subjected to microwave radiation for 3–7 min. The products were washed with water and HCl 10%, neutralized and dried at 110 °C.

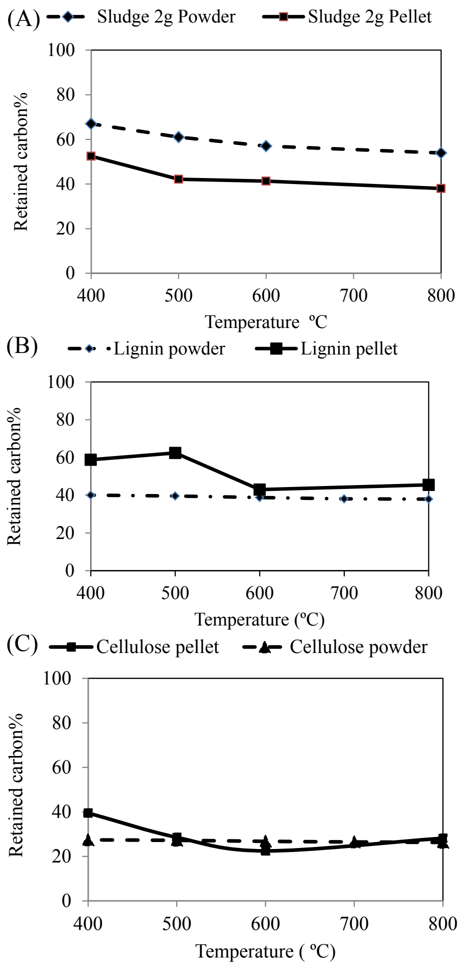

Fig. 4 – Effect of temperature on retained carbon % from pyrolysis of the sludge (A), lignin (B) and cellulose (C) in conventional electric furnace.

Table 3 – Effect of mass fraction of added KOH to dried sludge on retained carbon in microwave pyrolysis.

Mass fraction of KOH (%)	1	5	10
Retained carbon (PS50-50)	47	48	47
Retained carbon (PS70-30)	40	44	38

The Specific Surface Area (SSA) of activated carbon was measured using the Brunauer-Emmett-Teller (BET) method. Surface morphology of the char and activated carbon was analyzed using a Scanning Electron Microscopy (SEM) system (Hitachi S570).

3. Results and discussion

3.1. *Characterization of pulp mill sludge samples*

Two sludge samples (PS50-50 and PS70-30) were used to study the effect of sludge composition on pyrolysis. Table 1 shows the mass fractions of lignin, carbohydrates (cellulose and hemicellulose), extractives, and protein for the two sludge samples. PS50-50 and PS70-30 were very similar in their constituents except for their protein and lignin contents. PS70-30 contained less protein and more lignin compared to PS50-50 due to its lower secondary sludge content.

Table 2 shows the results of proximate and ultimate analyses of the dried sludge samples. Proximate analysis shows the composition of the biomass in terms of its main components i.e. fixed carbon, volatile matter, and ash contents, while the ultimate analysis gives the elemental compositions of the biomass. Volatile matters of a biomass consist of both condensable and non-condensable gases released when the dried biomass is heated. The solid remaining from this process is the sum of the fixed carbon and ash. The fixed carbon is the carbon in the solid form and is a fraction of the elemental carbon (total carbon) from ultimate analysis. PS50-50 had a higher mass fraction of elemental carbon (51%), a higher volatile matter but lower fixed carbon content compared to PS70-30. Thus, it is expected to get a higher yield from PS70-30 because of its higher mass fraction of fixed carbon. Both sludge samples had a low mass fraction of ash (4%) which is favorable for carbon production. The microwave-assisted pyrolysis yield of PS70-30 was 44%.

3.2. *Microwave-assisted pyrolysis with alkali metal hydroxides as microwave absorber*

In this work, KOH was used as a microwave absorber. Sludge, cellulose and lignin were not pyrolyzed in microwave oven due to their low microwave absorbability reported by Ref. [29]. Microwave absorbers would readily reach to a higher temperature and heat up the surrounding biomass through conduction. Microwave absorbers may assist the uniform heating of pulp mill sludge to produce a uniform char.

The shape of biomass is expected to affect the uniformity of produced char. Microwave-assisted pyrolysis was carried out for both powdered sludge and pellets with various mass fractions of KOH. With 1% of ground KOH, a complete pyrolysis of sludge pellets couldn't be achieved after 3 min when the power level was 1200 W (Fig. 2). Increasing KOH amount improved the degree of pyrolysis and the uniformity of pyrolysis product due to the high microwave absorbability and thermal conductivity of KOH. When the mass fraction of KOH was increased to 5%, a complete pyrolysis was achieved. Moreover, the amount of KOH affects the temperature of samples during microwave-assisted pyrolysis.

3.3. *Effect of the biomass sample shape on retained carbon*

The behavior of sludge during microwave-assisted pyrolysis was compared with that of cellulose and lignin. Fig. 3 shows the retained carbon (%) from cellulose, lignin, and sludge sample (PS50-50) in both powdered and pellet forms after microwave-assisted pyrolysis with KOH mass fraction of 5% at the power level of 1200 W. There seemed no significant difference in retained carbon% between powdered and pellet samples, which is significant since a compressed sample may lead to a greater productivity and easiness in material handling. The retained carbon from lignin (40–60%) was higher than that of the sludge (20–40%) as well as cellulose (15–30%), making lignin a more desirable precursor for char production. The retained carbon% didn't change significantly with pyrolysis time, suggesting that the pyrolysis process was complete after three minutes with the power of 1200 W. The large error bars are an indicator of non-homogenous heating of lignin and cellulose during microwave-assisted pyrolysis.

To compare with microwave-assisted pyrolysis, the pellet and powder samples were also pyrolyzed using the conventional electric furnace, without adding KOH. Fig. 4 shows the retained carbon from cellulose, lignin and sludge at various temperatures (400–800 °C). The sludge's behavior was quite different from lignin and cellulose. First, the retained carbon from the powdered sludge was substantially higher than the pellet sludge, while the opposite was observed with lignin and no difference was observed with cellulose. The retained carbon from pellet sample was less than that from the powdered one, which was observed and explained by Ref. [30]. They suggested that faster release of gases and a shorter contact

Table 4 – Mass fractions of dry sludge (gas, liquid, and char) and carbon in char.

Mass fractions of dry sludge (%)	PS50-50			PS70-30		
	3 min	5 min	7 min	3 min	5 min	7 min
Gas	40 ± 4	43 ± 2	43 ± 2	48 ± 3	50 ± 3	52 ± 1
Tar and liquid	25 ± 1	26 ± 1	21 ± 1	26 ± 2	24 ± 2	23 ± 1
Char	35 ± 3	31 ± 4	36 ± 2	26 ± 3	24 ± 2	25 ± 3
Mass fraction of carbon in char	62 ± 2	67 ± 0	63 ± 3	62 ± 3	66 ± 4	70 ± 2

Table 5 – Mass fractions of dry feedstock (%) after microwave pyrolysis from literature and this work.

Dry feedstocks	Microwave pyrolysis conditions	Char (%)	Liquid (%)	Gas (%)	Reference
Wood sawdust	1200 W, 10 min	43	47	10	[31]
Oil palm shell	1000 W, 25 min	70	20	10	[32]
Macroalgae waste	1000 W, 6 min	28	35	37	[33]
Pulp mill sludge (PS50-50)	1200 W, 5 min	31	26	43	This work

time between the gas phase and the char bed can lower carbon retention from the gas phase. The char obtained from the powdered sludge had more elemental carbon compared to the pellet one, which shows the release of carbon compounds during pyrolysis of sludge pellets. The reason for the different behavior of lignin and cellulose is not clear at this point, although both of them contain less volatile matter compared to the sludge. As expected, the retained carbon from the sludge decreased with temperature. The temperature dependence of retained carbon of lignin or cellulose was much weaker. This finding suggests that lignin and cellulose are more readily pyrolyzed than the sludge at relatively low temperatures.

Overall, the retained carbon from the sludge varied from 40 to 60%, which is about 20% higher than those obtained with microwaves. On the other hand, 40–60% of carbon was retained from lignin, similar to that of microwave-assisted pyrolysis. The retained carbon from cellulose was again the lowest (20–30%) and similar to that with microwaves. Also it can be concluded that pulp mill sludge could not be treated as a simple mixture of lignin and cellulose in term of its behavior during pyrolysis.

At temperatures higher than 400 °C, KOH can oxidize carbon, which could lower the retained carbon% [21]. To quantify the effect of KOH on the retained carbon%, various mass fractions of KOH (1–10%) were added two sludge samples and 7 min of pyrolysis were conducted. The retained carbon (%) was measured and the results are shown in Table 3. For both PS50-50 and PS70-30, the effect of KOH mass fraction (1–10%) on the retained carbon% seems insignificant. The KOH weight was remained constant during pyrolysis. Hence, the observed lower retained carbon from microwave-assisted pyrolysis of sludge samples is likely due to the faster heating rate which may lead to a faster rate of the volatile release. Microwave and conventional pyrolyses are inherently different in process conditions and retained carbon% would depend on these conditions.

3.4. *Comparison between two pulp mill sludges (PS50-50 and PS70-30)*

The two samples were pyrolyzed using the microwave oven and the conventional furnace, respectively. In microwave-assisted pyrolysis, powdered sludge samples were mixed with 5% KOH and power level of 1200 W. Table 4 shows the mass fraction of gas, liquid/tar and char from pyrolysis and mass fractions of carbon in char produced by microwave pyrolysis of PS50-50 and PS70-30. The liquid fraction was produced and distilled during the pyrolysis and it was reported as a part of tar. After three minutes of pyrolysis, 40–50% of the dried biomass was turned into gas product and 21–26% into liquid and tar products. The char yield was higher for PS50-50, while the mass fractions of carbon in chars were similar for both sludge samples in microwave-assisted pyrolysis. The temperature of 20 g dried sludge with a KOH mass fraction of 5% can reach to 450 and 700 °C for the medium (600 W) and high (1200 W) power, respectively [29].

Table 5 shows the comparison of the mass fractions of microwave-assisted pyrolysis from this work with literature data for different feedstock. The properties of raw materials and operating parameters affect the pyrolysis yields. Oil palm shell had a high mass fraction of char 70% compared to the other reported raw materials. However, the mass fraction of fixed carbon in pulp mill sludge was the same as oil palm shell (20%). Microwave absorbers were added to the macroalgae, oil palm shell, and pulp mill sludge samples.

Fig. 5 shows the difference in retained carbon between two sludge samples – PS50-50 and PS70-30. After 3 min of microwave-assisted pyrolysis, 42% and 35% of carbon were retained from PS50-50 and PS70-30, respectively. Prolonging time from 3 to 9 min didn't result in any significant change in retained carbon%. These results indicate that with KOH mass fraction of 5% and the power level of 1200 W, the powdered sludge can be completely pyrolyzed in three minutes. More carbon can be retained from PS50-50 which contained more secondary sludge. This phenomenon could be because of the higher protein content in the PS50-50. A study on pyrolysis of

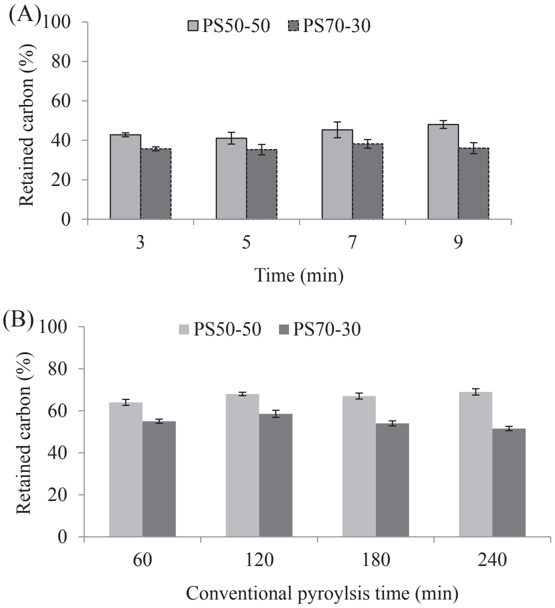

Fig. 5 – Comparison between PS50-50 and PS70-30 in retained carbon (%) during microwave pyrolysis (A) and conventional pyrolysis (B) with KOH mass fraction of 5%.

Table 6 – Porosity and yield of activated carbon produced from pulp mill sludge (PS50-50) using microwave-assisted combined pyrolysis and activation.

Activation conditions	Yield (%) of activated carbon	BET-SSA ($m^2 g^{-1}$)
3 min, 0.05NaOH: Sludge, power 1200 W	35	56
3 min, 1NaOH:1sludge, power 1200 W	19	500
5 min, 1NaOH:1sludge, power 1200 W	18	490
5 min, 2NaOH:1sludge, power 1200 W	13	660
7 min, 1NaOH:1sludge, power 1200 W	16	424

carbohydrates, lipids, and proteins showed that proteins tend to be converted into solid residues compared to lipids and carbohydrates [34].

Fig. 5(B) shows the retained carbon from two sludge samples using the conventional furnace. The pyrolysis was carried out at 400 °C in 1–4 h. Again, the retained carbon% was consistently higher for PS50-50 (65–70%) than that for PS70-30 (45–55%). Increasing time from 1 to 4 h didn't lead to any significant change in retained carbon%. The higher mass fraction of retained carbon in the char from PS50-50 was not expected, since it had a higher volatile matter and a lower fixed carbon. On the other hand, PS50-50 contained more secondary sludge and protein, which might be responsible for its higher retained carbon%. However, it is clear that a large fraction of the carbon in volatile matters was retained in the char during pyrolysis with microwave oven and conventional furnace.

3.5. *Microwave-assisted combined pyrolysis and activation*

Due to the dual roles of alkali metal hydroxides as microwave absorbers and activation agents, combining pyrolysis and activation is recommended to make the production of activated carbon a one-step process. To demonstrate the feasibility, pulp mill sludge sample (PS50-50) was mixed with NaOH at a mass ratio of 1:1 and subjected to microwave radiation. For the activation of pulp mill sludges, NaOH was found to be more effective in pore development than KOH [29]. The BET-SSA values of KOH-activated carbon produced with microwave-assisted combine pyrolysis and activation were between 150 and 350 $m^2 g^{-1}$. Table 6 shows the BET-SSA values of samples obtained from this one-step activation process. The BET-SSA of the char from microwave – assisted pyrolysis with 5% NaOH, as a microwave absorber, was only 56 $m^2 g^{-1}$. The results of combined pyrolysis and activation show that a BET surface area of 500 $m^2 g^{-1}$could be achieved after three minutes of activation with microwaves. Increasing the time to seven minutes resulted in lower SSA values, likely caused by the enlargement of pores. A preliminary test showed that doubling the amount of NaOH was able to increase the SSA from 490 to 660 $m^2 g^{-1}$. Although the feasibility of one-step process was demonstrated, the process itself was not optimized in terms of yield after five minutes of one-step activation, the yield was about 20%. The yield from the two-step process was typically higher [29].

The morphology of the sludge-derived char and activated carbon was investigated using a scanning electron microscopy (SEM). Fig. 6A and B illustrate the porous structure of the char and activated carbon produced from the sludge with microwaves, respectively. Both samples were produced under 1200 W and 5 min microwave heating. The ranges of pore sizes in the produced chars and activated carbon were very different. In this work, large pores in the char were in micrometers, while smaller pores in nanometers were visible in the activated carbon sample.

4. Conclusions

Microwave-assisted pyrolysis of pulp mill sludge with using KOH as a microwave absorber is an efficient process for char production. Adding a KOH mass fraction of 5% enabled a complete pyrolysis of the sludge in a few minutes. The retained carbon with microwaves was 20% lower than that of conventional heating due to the faster release of volatiles with microwaves. The secondary sludge with higher protein contents yielded more char than the primary sludge. Because proteins can be converted into char more than carbohydrates and lipids. Microwave-assisted combined pyrolysis and

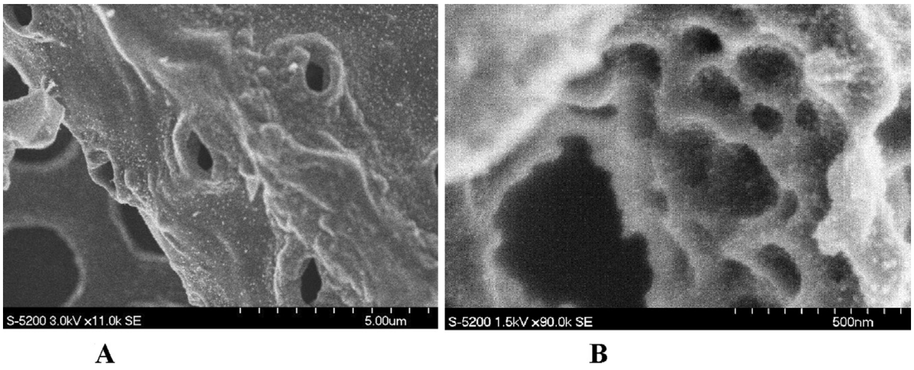

Fig. 6 – SEM micrographs of sludge-derived char (A) and activated carbon (B) produced with microwaves (Char micrograph is at 5 μm scale and activated carbon at 500 nm).

activation of the sludge is feasible due to the dual roles of alkali metal hydroxides as activating agent and microwave absorber. With the combined one-step process, activated carbon with a BET specific surface area of 660 $m^2 g^{-1}$ was produced.

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